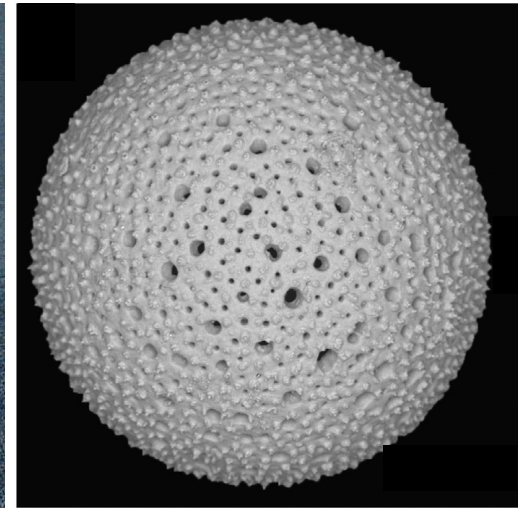
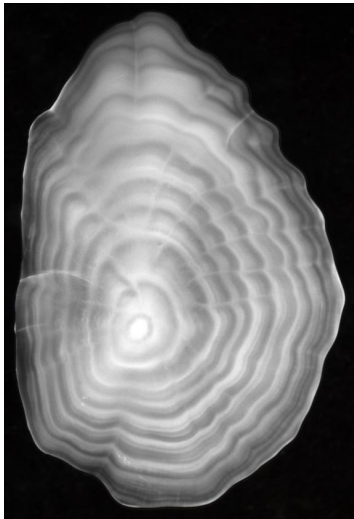


MICROANALYSIS OF OXYGEN ISOTOPE RATIOS II: BIOCARBONATES

John Valley
and *MANY* others

I: Silicates (Tomorrow)

University of Wisconsin-Madison

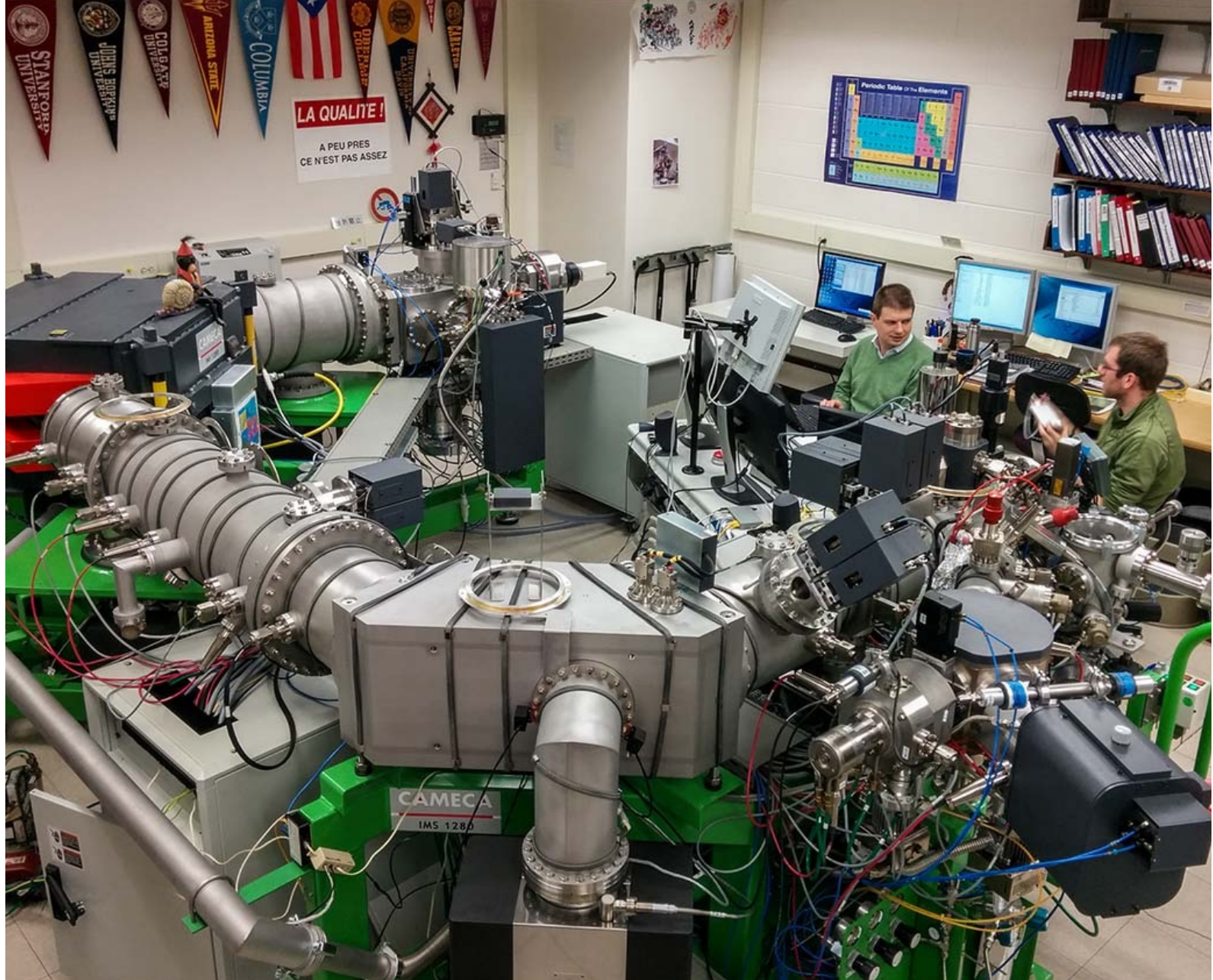
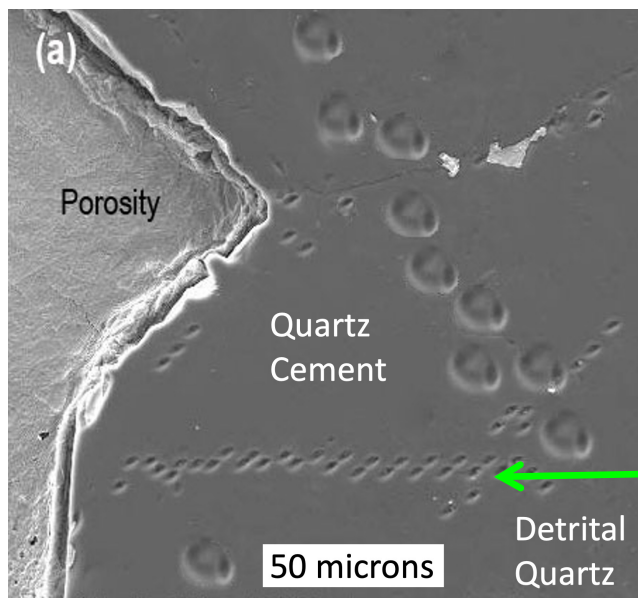
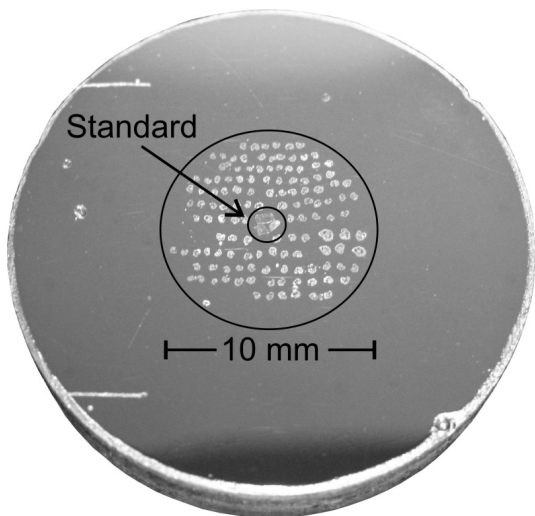


WiscSIMS is funded by
NSF-EAR as a National Facility





SIMS
IMS-1280



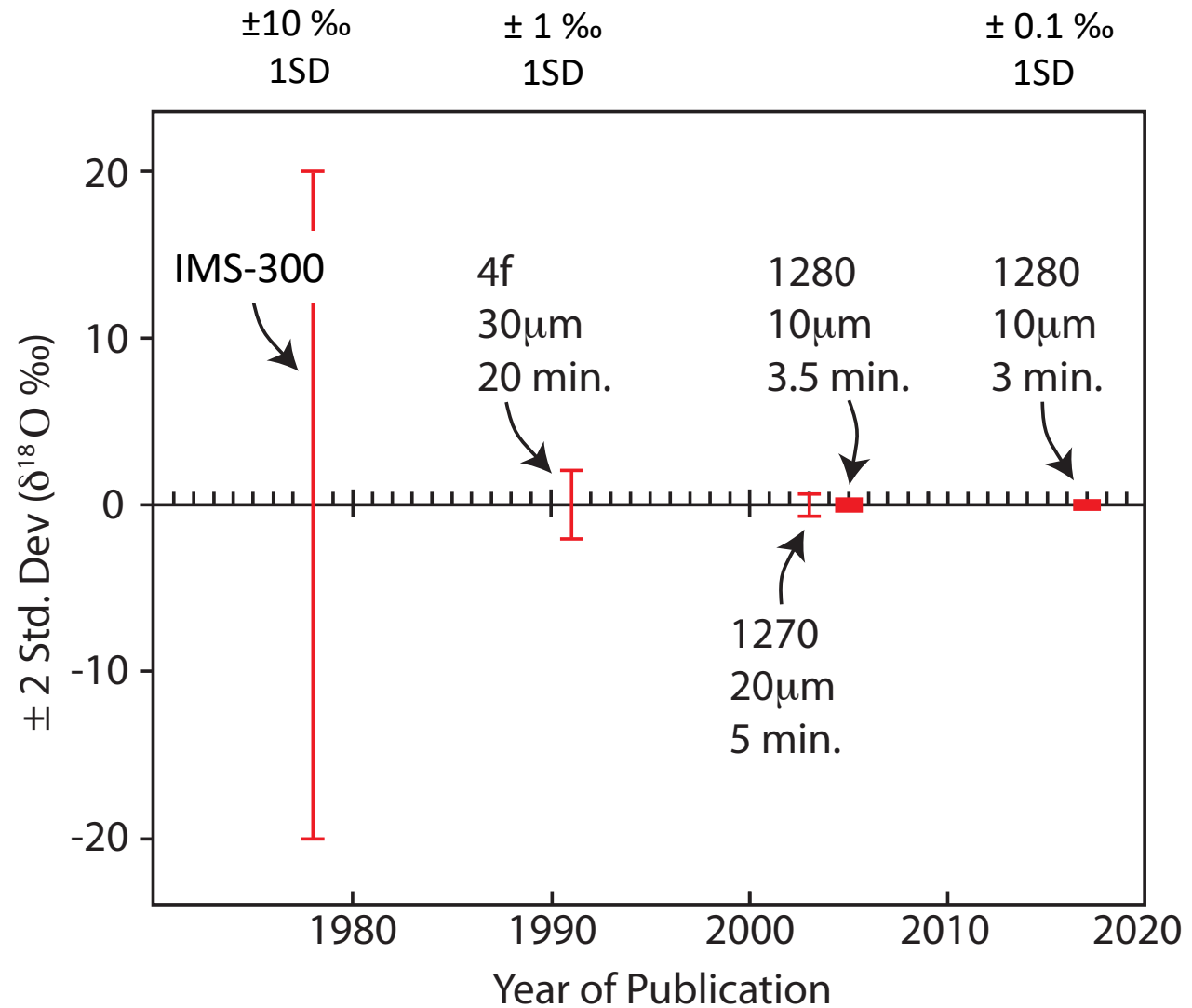
In situ analysis
1-10 micrometer spot
 10^{-9} - 10^{-12} g

Million to billion times smaller than GSMS!
Spatially resolved

Oxygen Isotopes- SIMS

40 years of Improvement

- Analytical Precision
- Spot size
- Speed
- Reliability
- Accuracy



Giletti et al. 1978
 Valley & Graham 1991
 Cavosie et al. 2003, 2005
 Tenner, Kita et al. 2017

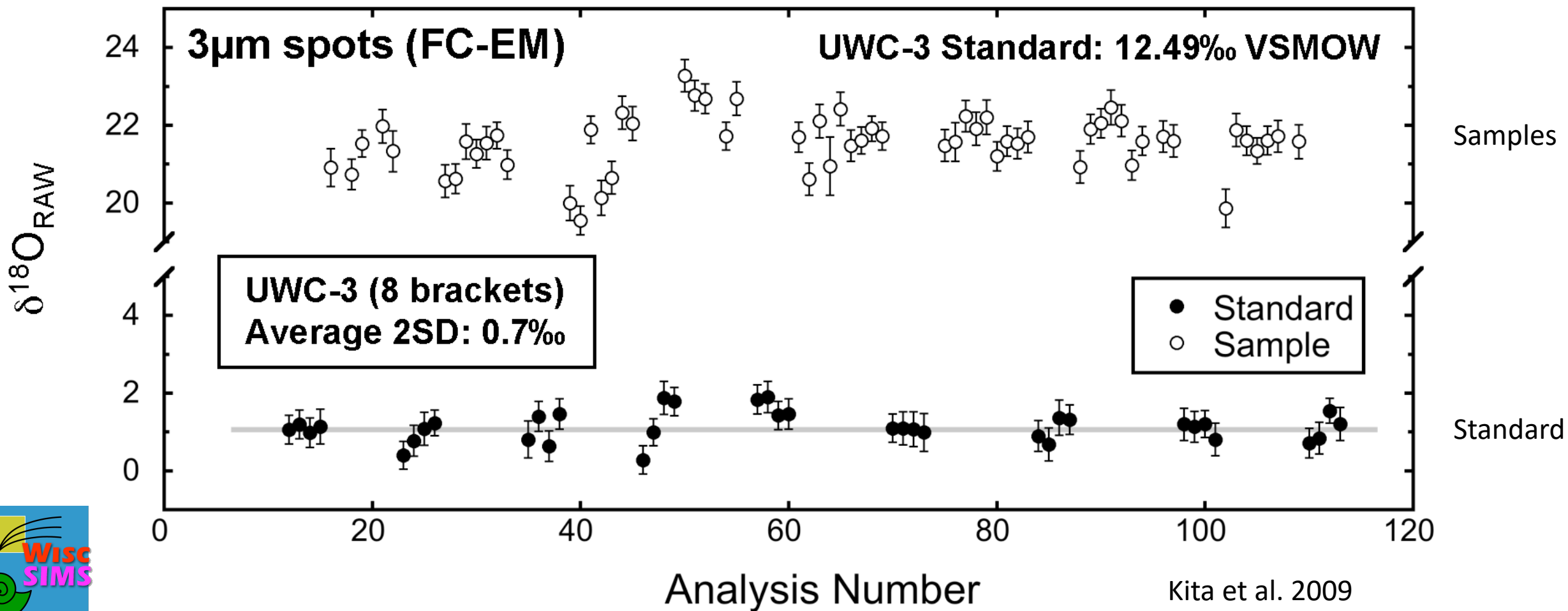


$\delta^{18}\text{O}$

Calcite

3- μm spot, FC-EM

10 μm spot: $\pm 0.1\text{‰}$ 1SD
3 μm spot: $\pm 0.3\text{‰}$ 1SD
1 μm spot: $\pm 1\text{‰}$ 1SD

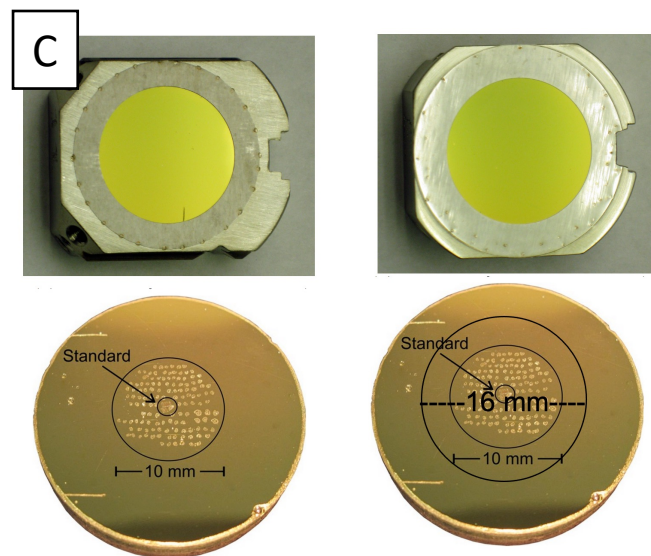
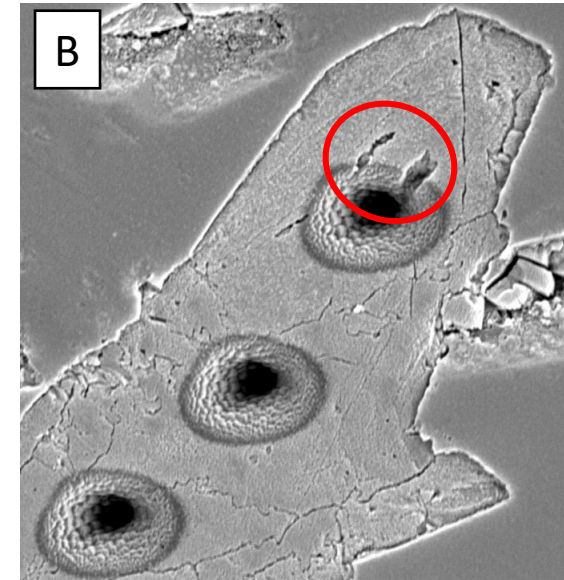
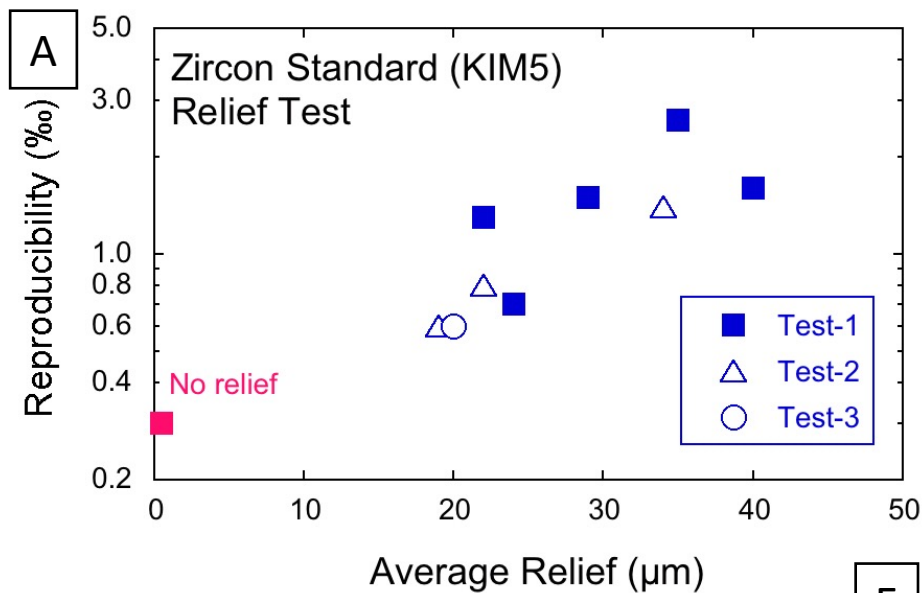


Sample Preparation

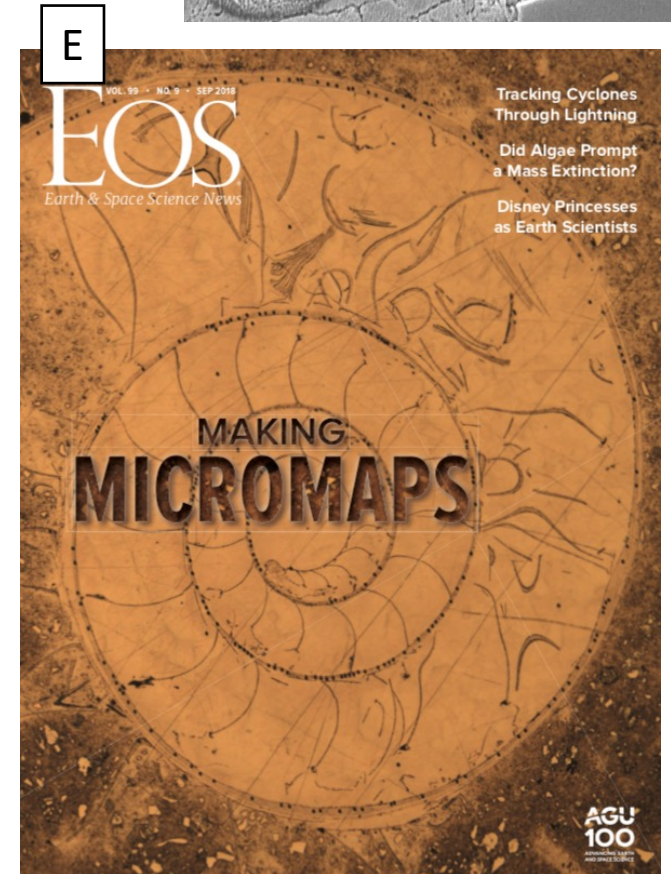
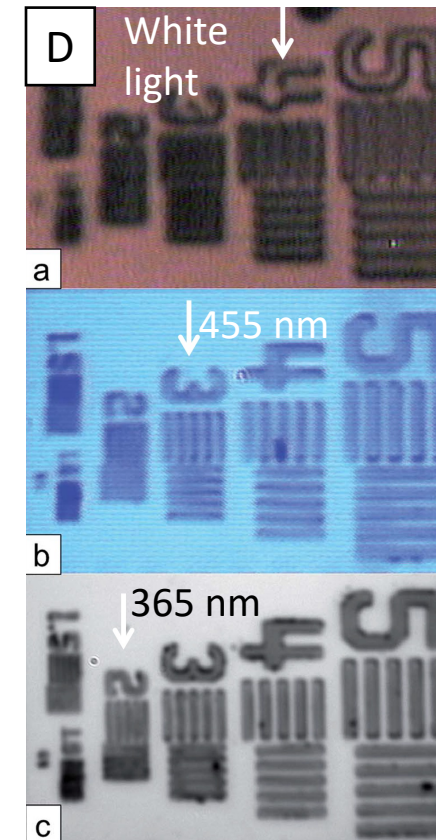
- A. Minimize surface relief, Kita et al. 2009
- B. Examine SIMS pits by SEM
- C. Larger sample holder, Peres et al. 2013
- D. UV viewing optics, Kita et al. 2015
- E. QGIS, Linzmeier et al. 2019

Automated analysis

Standards



Average Relief (μm)



$\delta^{18}\text{O}$ IMF (bias)

Accuracy requires standards (RMs)

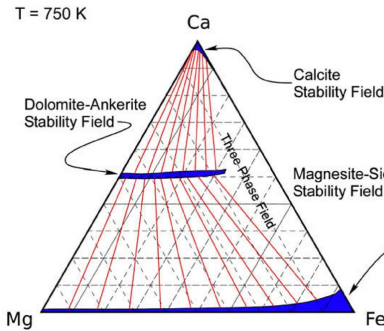
Matrix effect of Ca-Mg-Fe carbonates

30 Inorganic Carbonate Standards

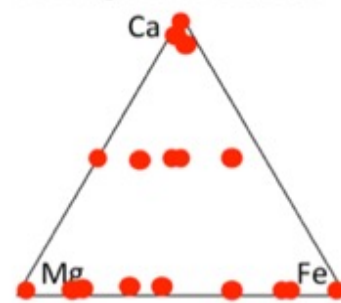


Valley 2022 GSA

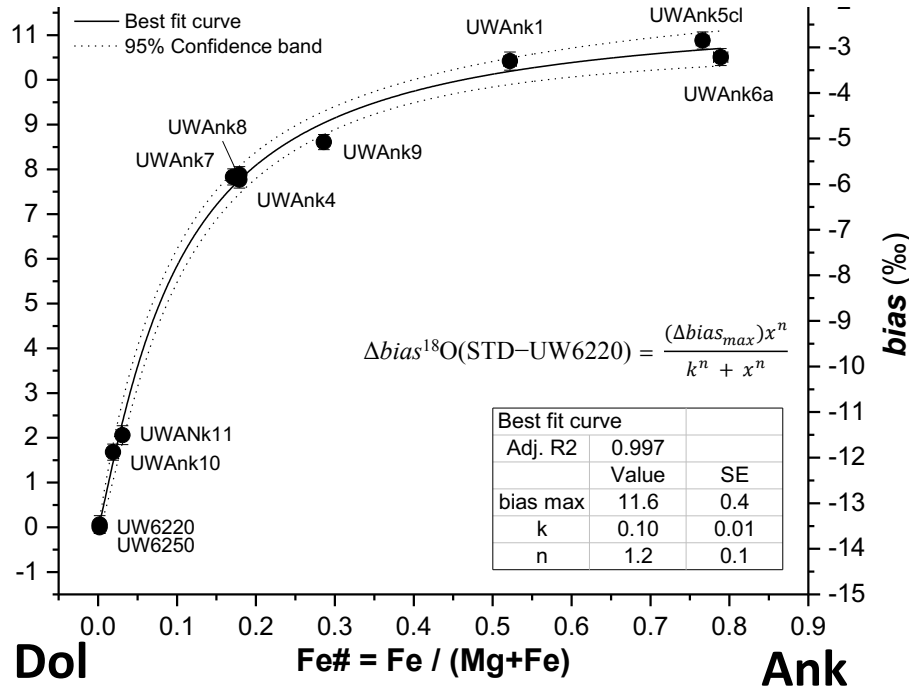
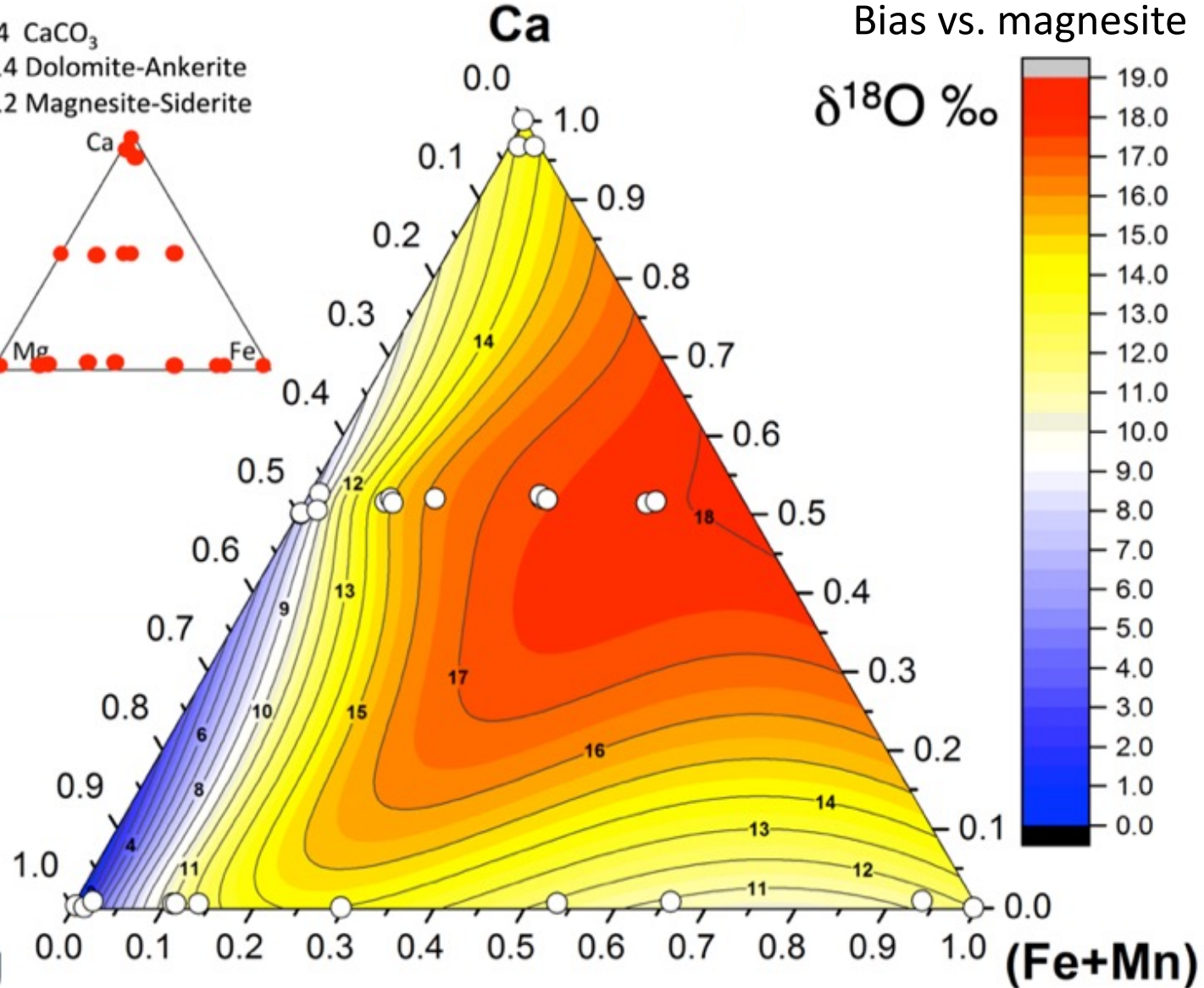
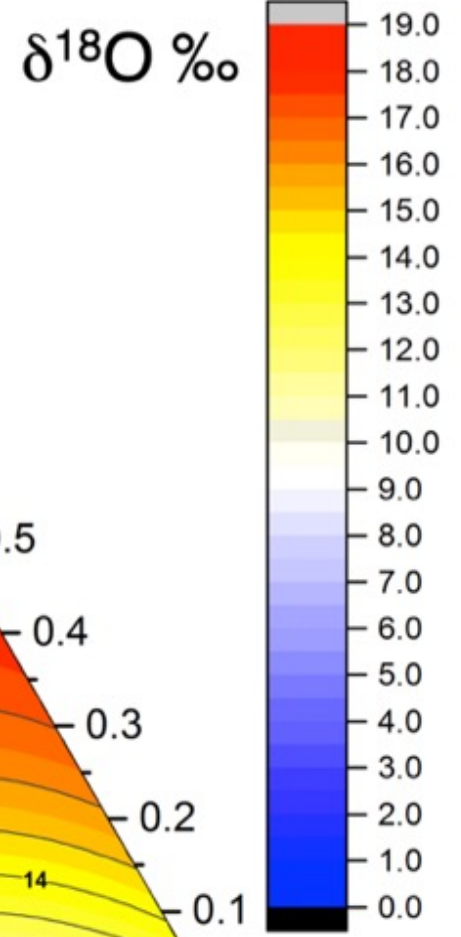
Valley and Kita 2009
Sliwinski et al. 2016a,b
Kitajima et al., unpd



4 CaCO_3
14 Dolomite-Ankerite
12 Magnesite-Siderite

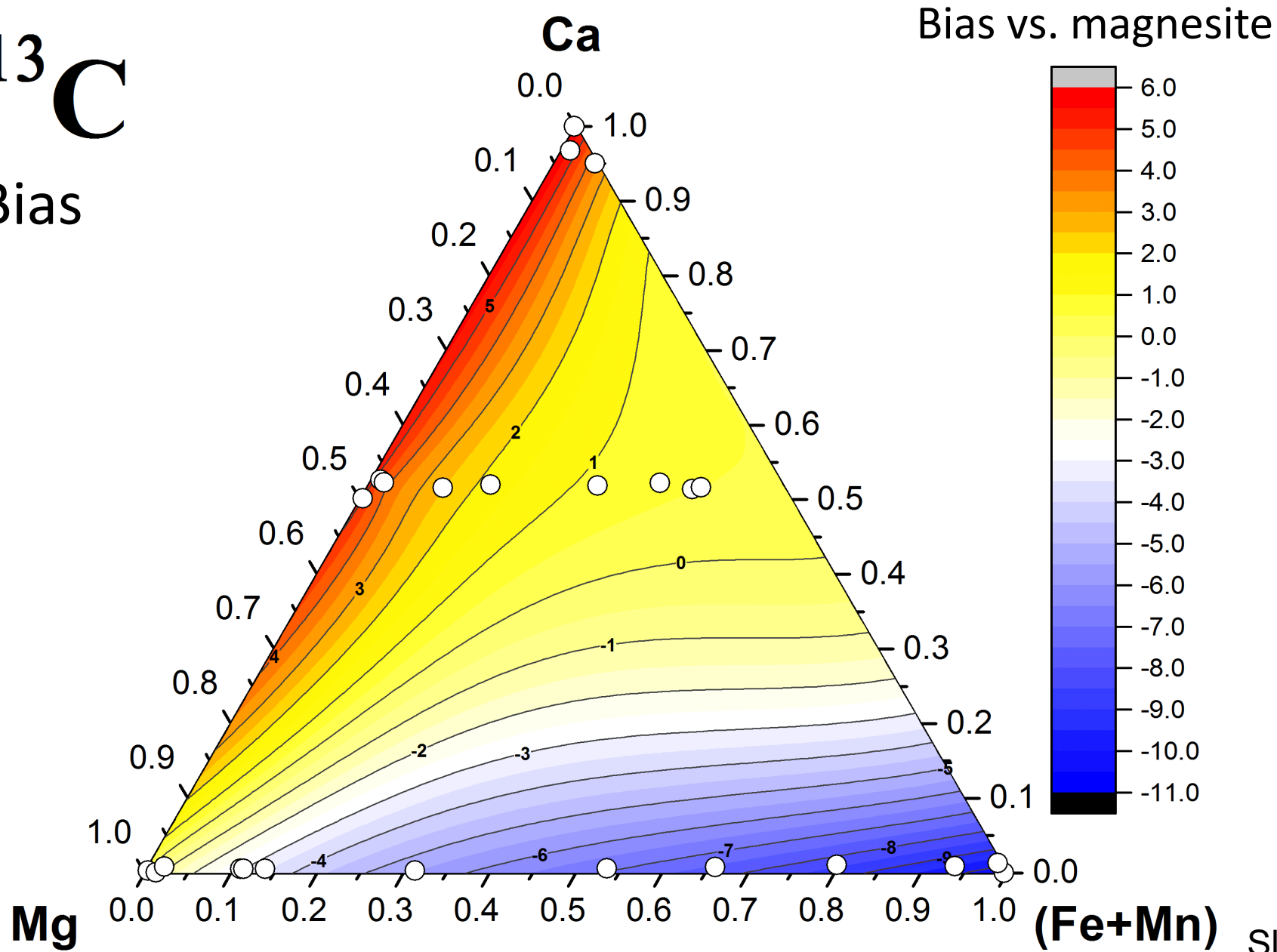


Bias vs. magnesite



$\delta^{13}\text{C}$

Bias



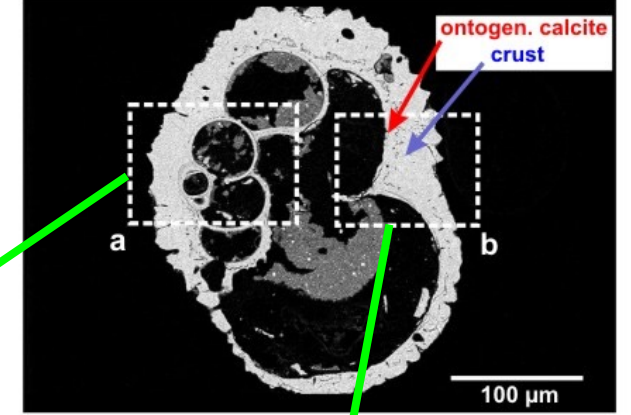
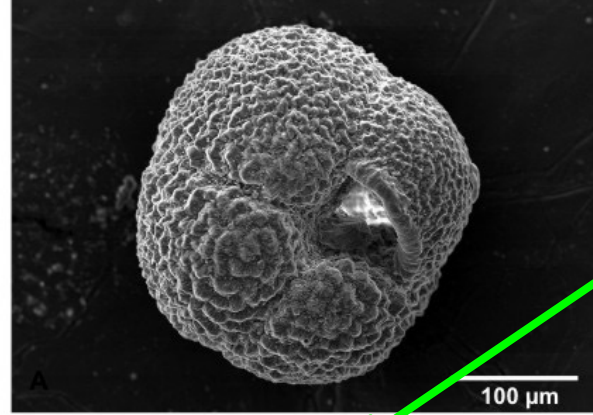
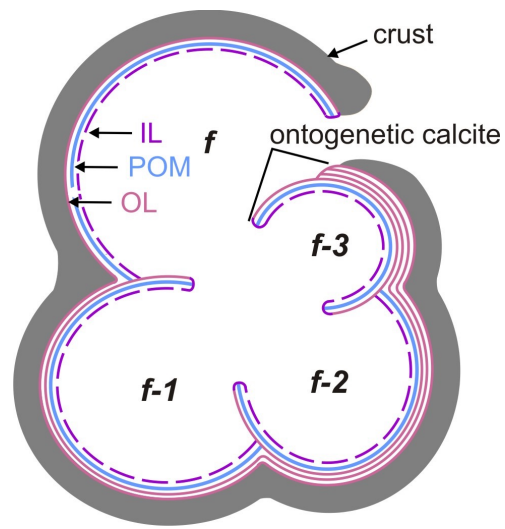
Sliwinski et al. 2016a,c
Kitajima et al., unpd



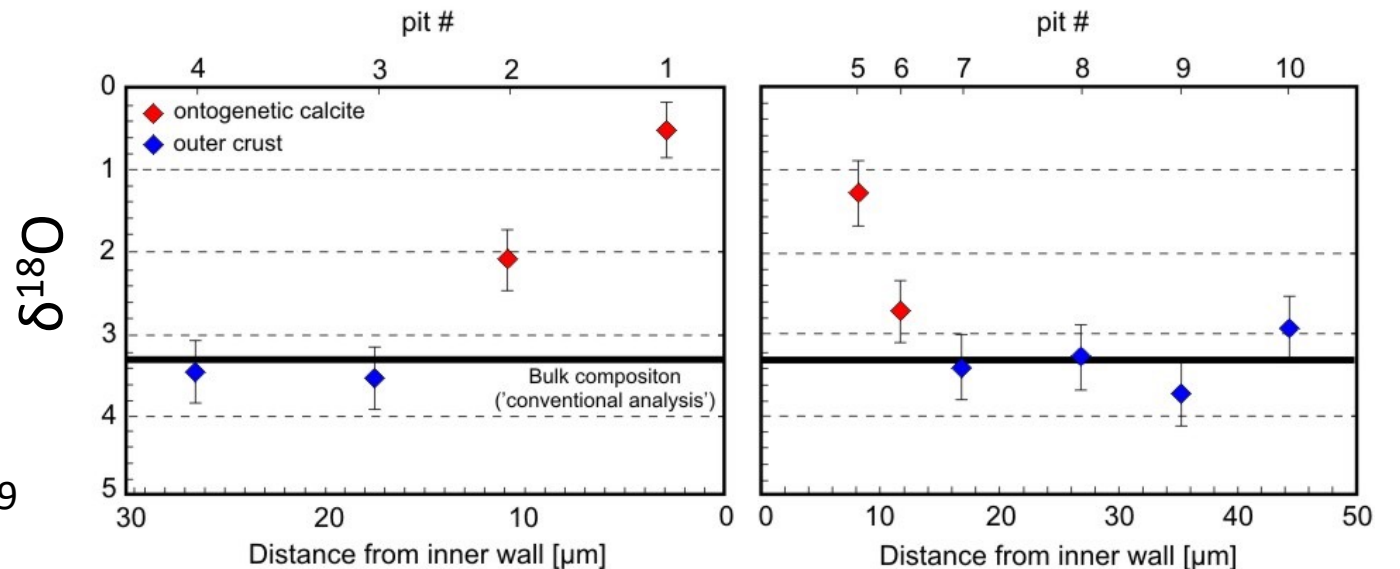
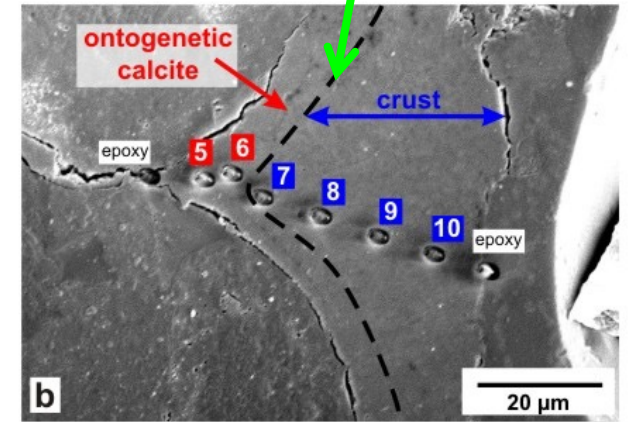
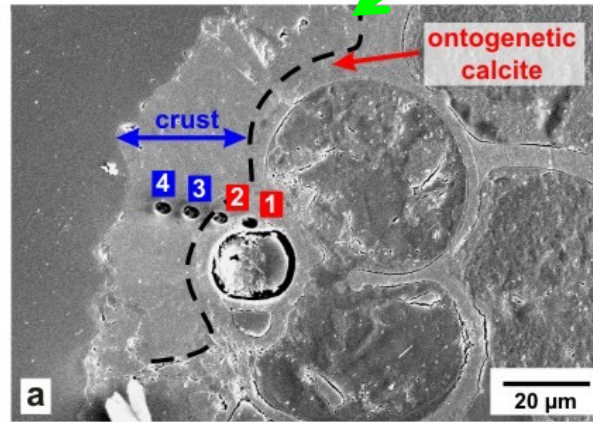
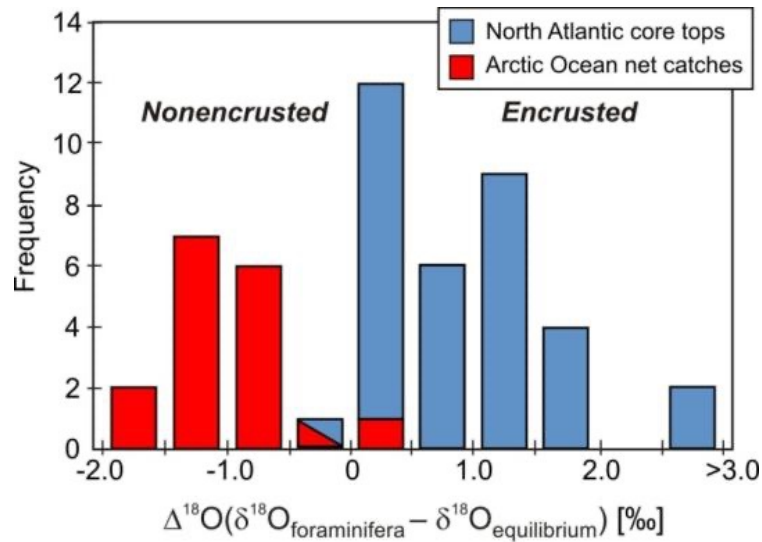
Foraminifera

N. pachyderma (sin.)

Core top, N. Atlantic



Vital Effects



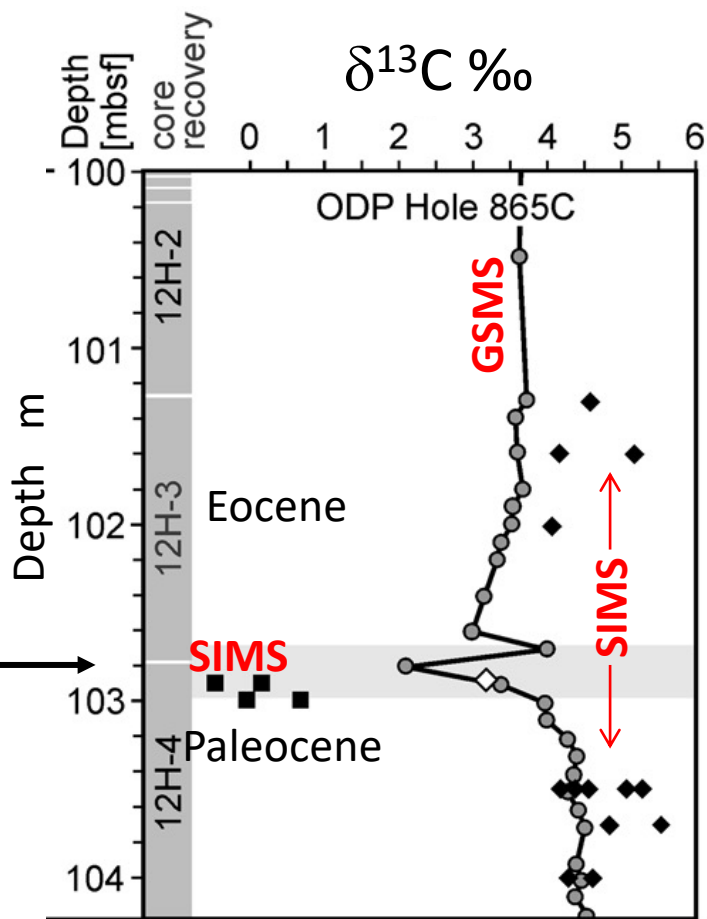
Kozdon et al. 2009



$\delta^{13}\text{C}$ - Paleocene-Eocene Boundary

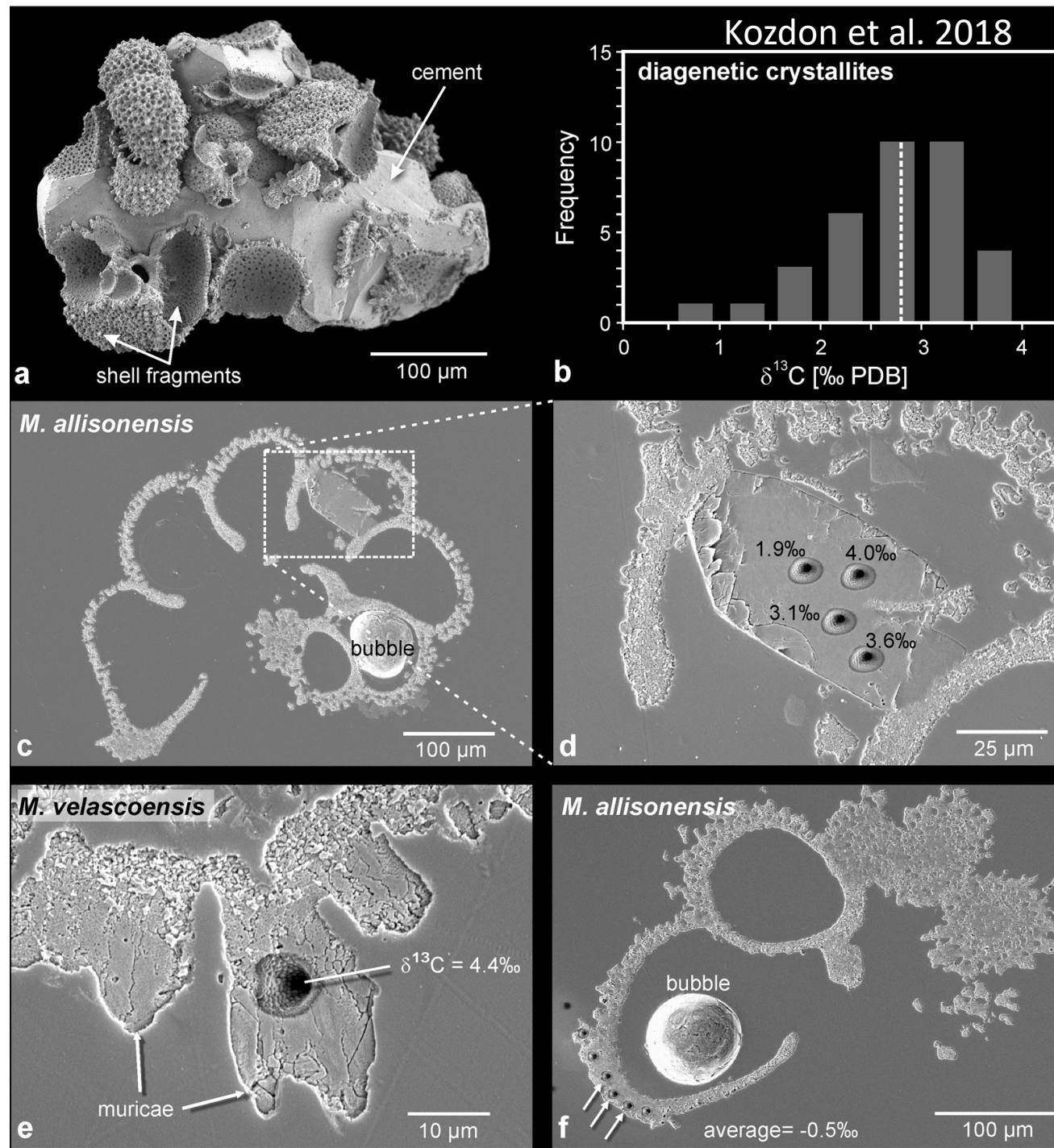
PETM Hothouse Event

CIE = Carbon Isotope Excursion



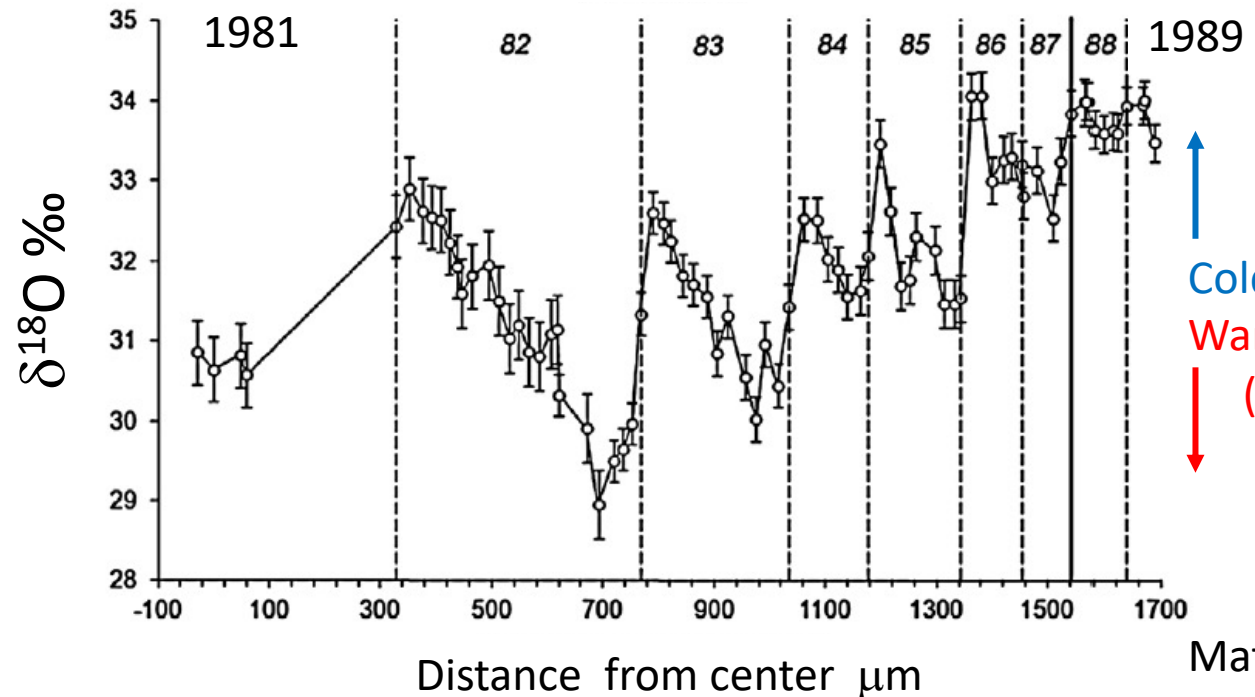
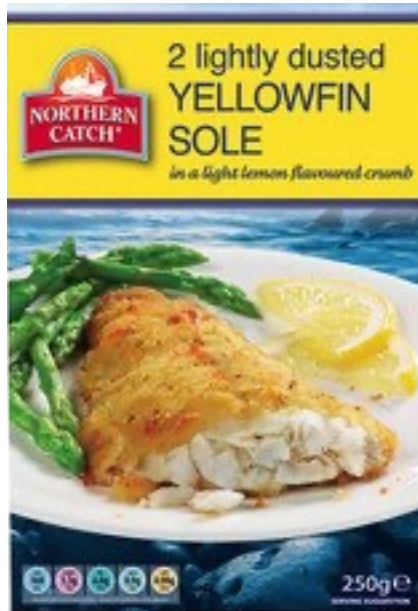
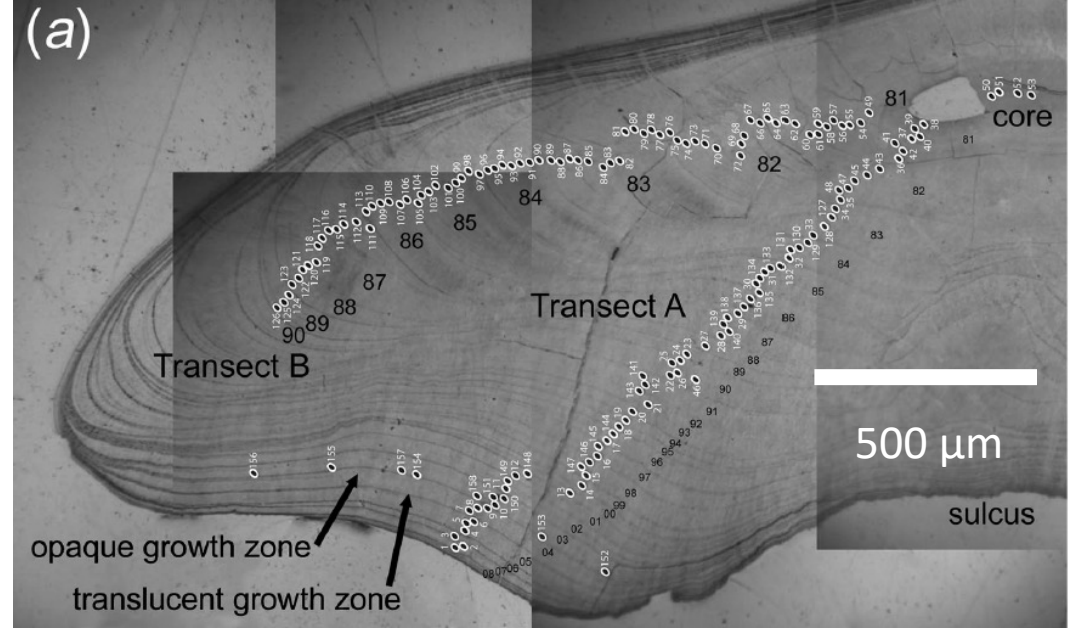
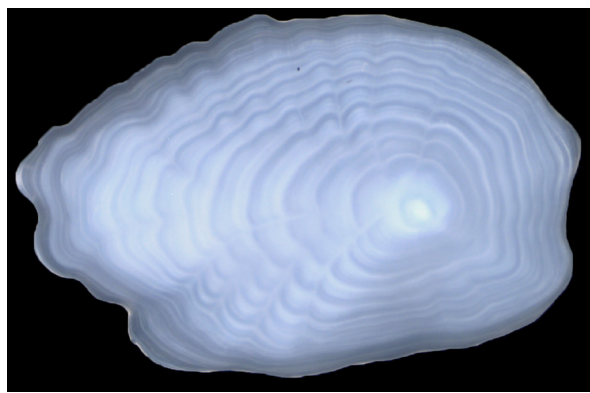
GSMS- $\delta^{13}\text{C}$ excursion CIE $\sim 2.5 \text{ ‰}$
Bralower et al. 1995

SIMS- $\delta^{13}\text{C}$ excursion CIE = 4.6 ‰
Kozdon et al. 2018



Otoliths

aragonite
Yellowfin Sole
Bering Sea



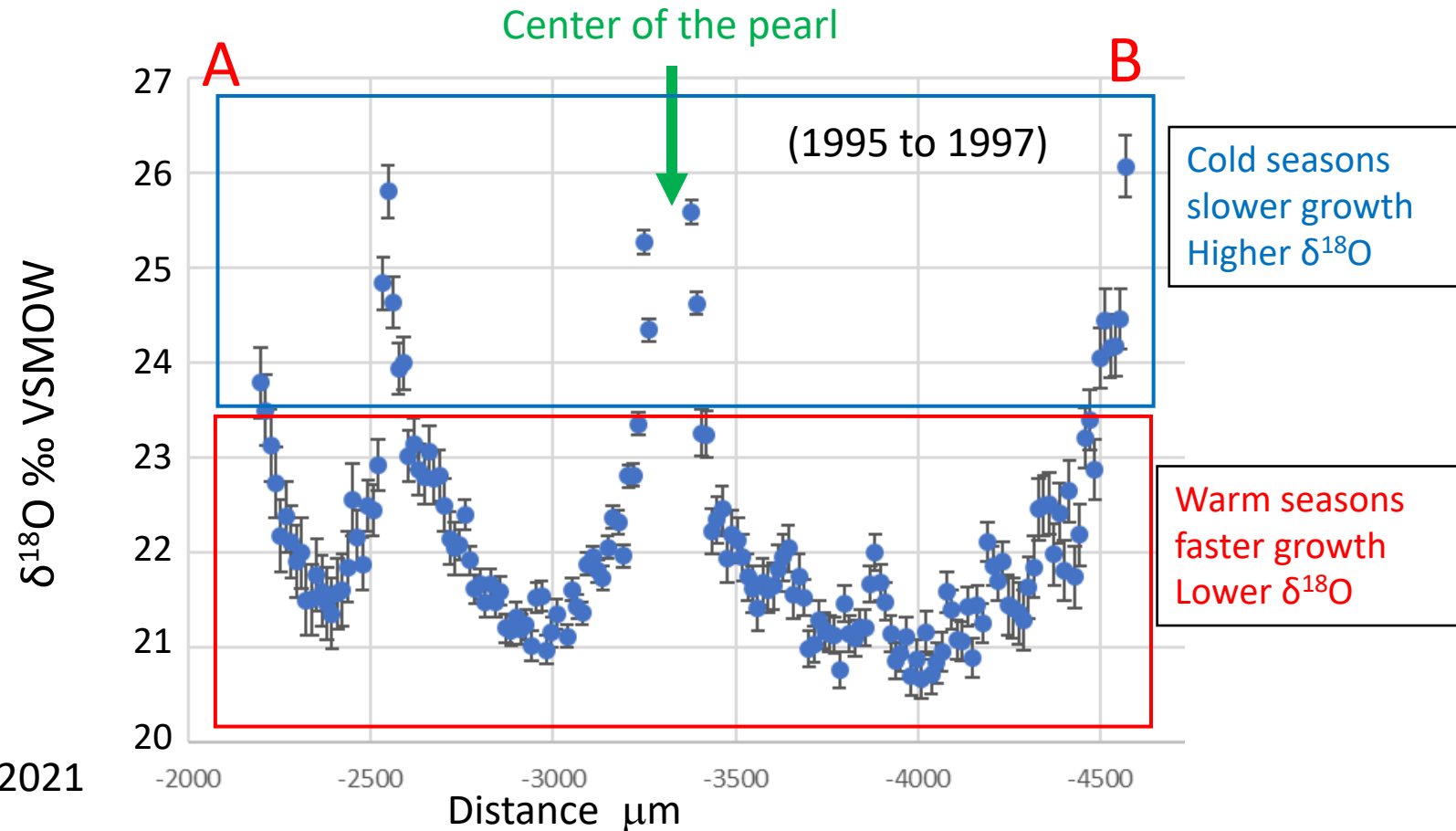
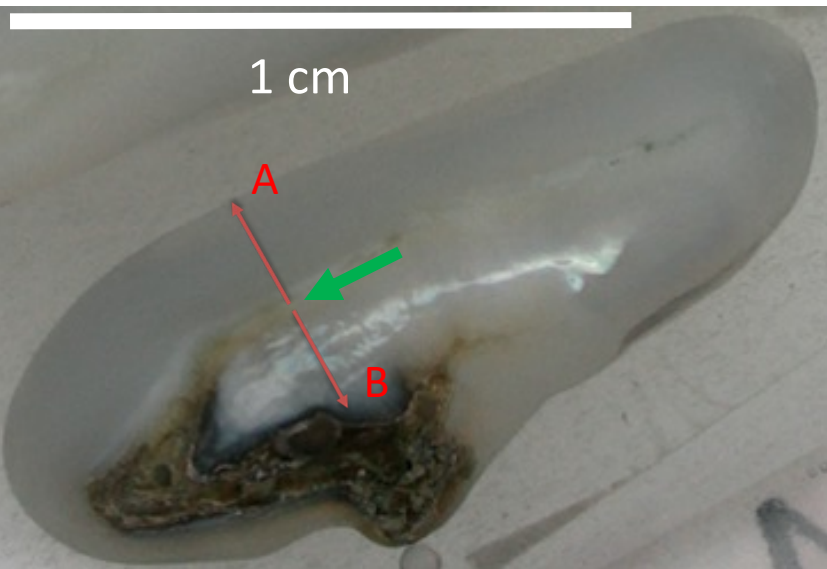
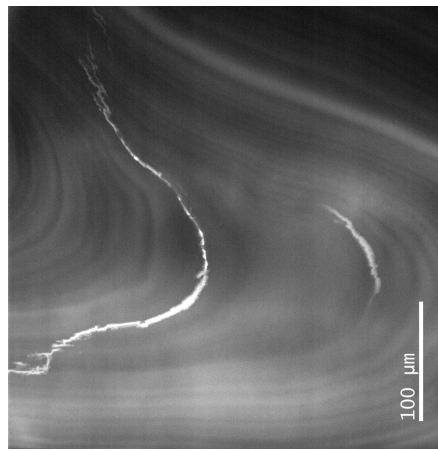
Pearls

Aragonite

Freshwater cultured, 1995 to 1997

American Pearl Co., Kentucky Lake

Seasonal record of water T & $\delta^{18}\text{O}$



GIA®



Farfan et al. 2021

Accuracy vs. Precision

Precision of SIMS measurements

Spot-to-spot reproducibility
on homogeneous standard

Accuracy of SIMS measurements

Sample preparation

Post-analysis: image pit, ion yield, OH

Bias (IMF): matrix effects

Reference standards

calibrated & homogeneous

chemical & structural match to samples

Biocarbonates are not Pure CaCO_3



Offset- Biocarbonates- CaCO_3

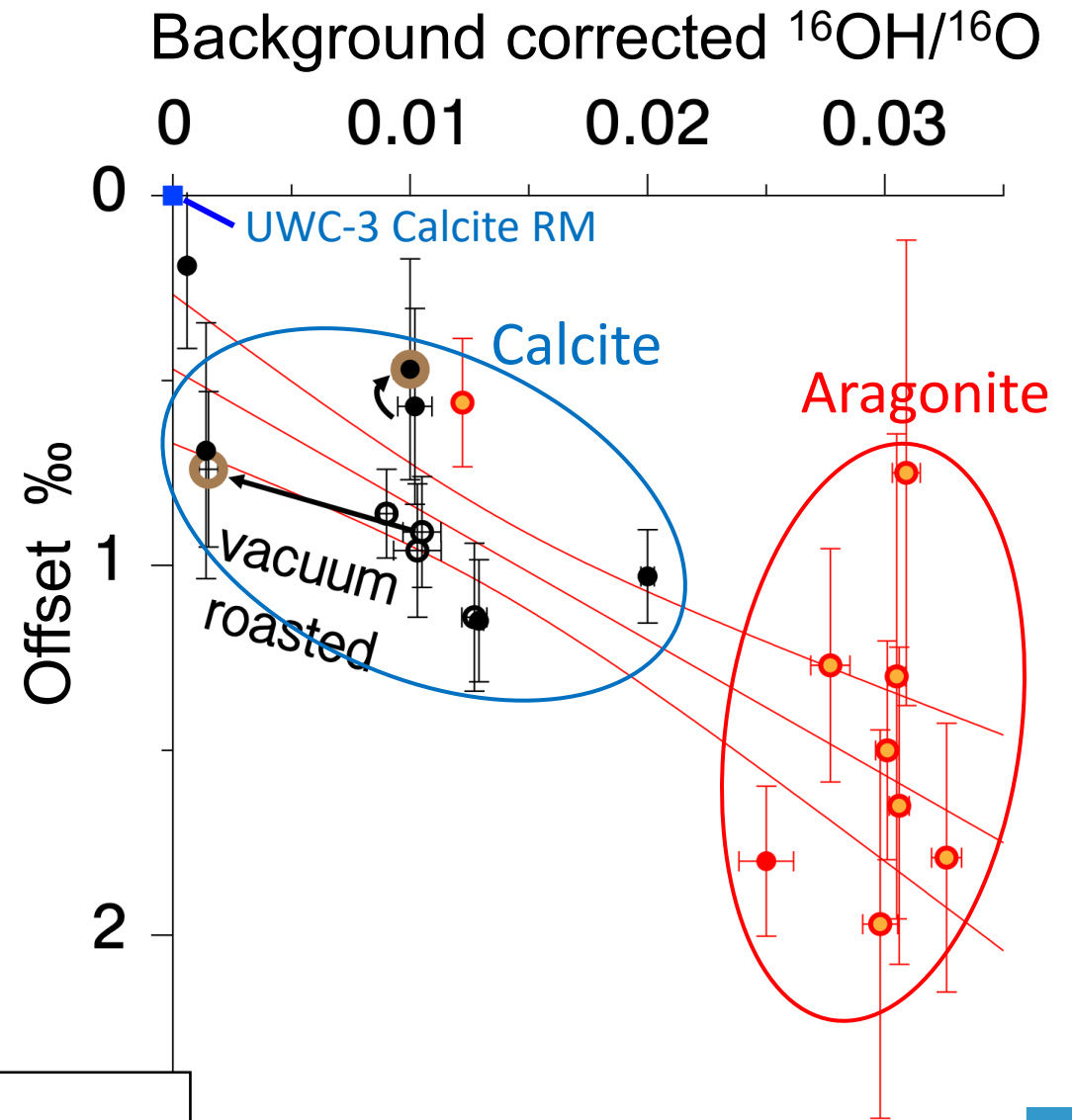
$$\text{Offset} = \delta^{18}\text{O}_{\text{GSMS}} - \delta^{18}\text{O}_{\text{SIMS}}$$

Background corrected OH/O ratios
background subtracted,
but not calibrated by RMs

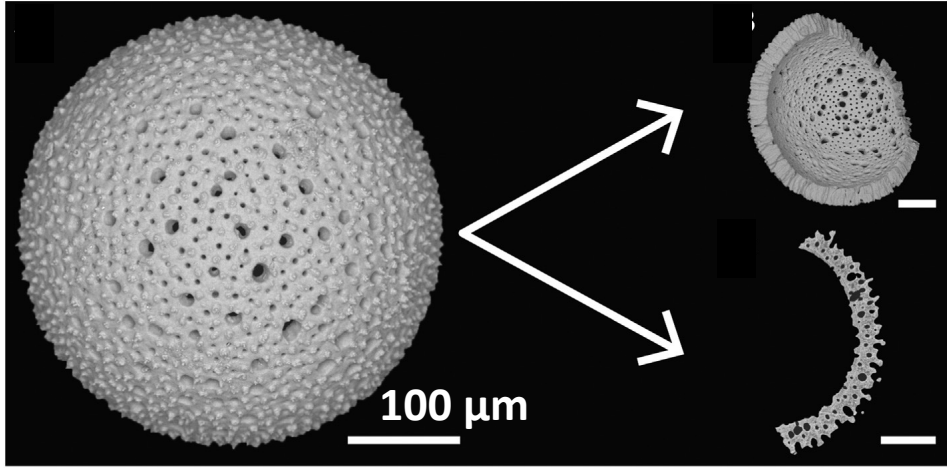
Biocarbonates
Age < 75 ka
N=4113 SIMS
N=1117 IRMS

Orland et al. 2015 AGU, 2017
Linzmeier et al. 2016
Wycech 2017 PhD
Orland 2012 PhD
Helser et al. 2018
Keul et al. 2016 AGU

Standards must match samples
Biocarbonates are not Pure CaCO_3
Analysis of minor elements, water and OM in CaCO_3

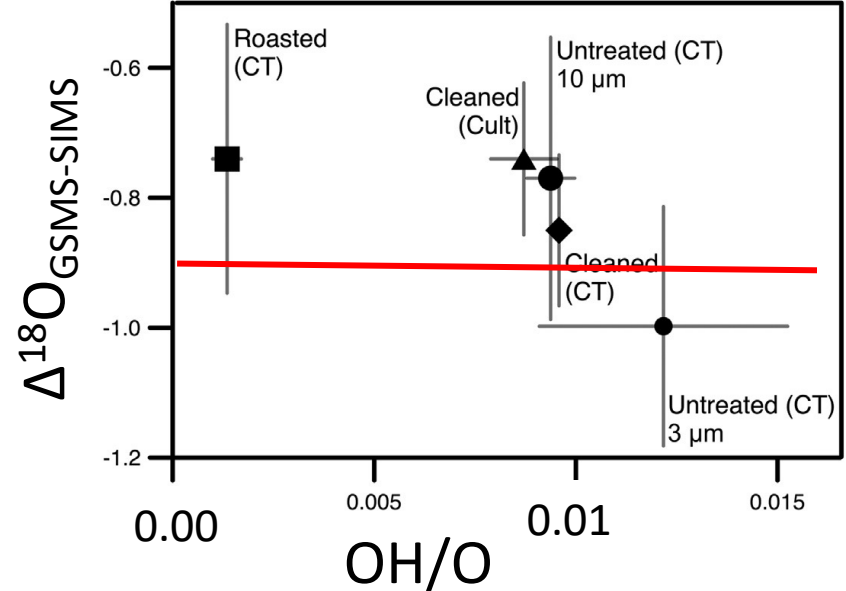
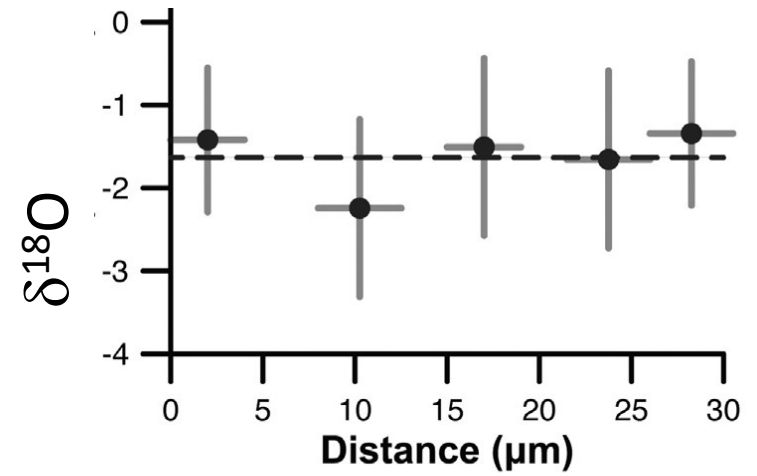
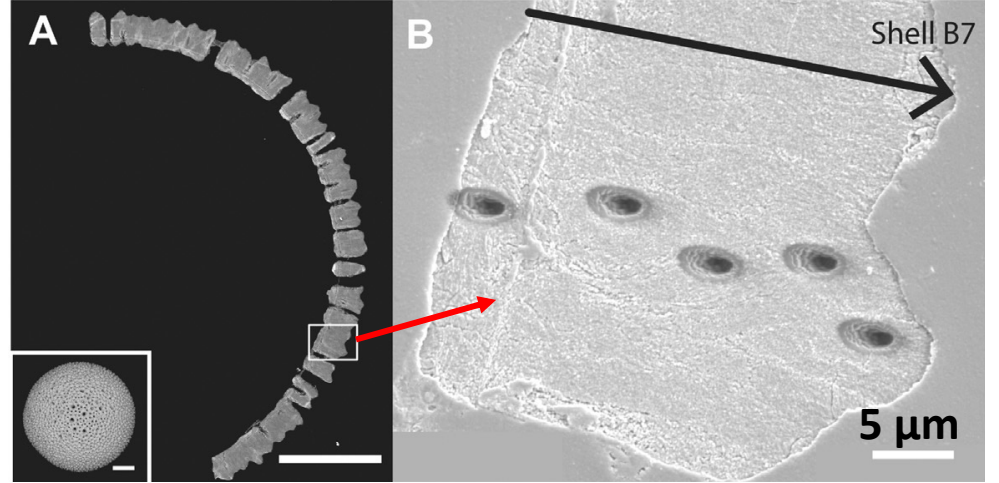


Orbulina universa (calcite, modern)



Acid dissolution
GSMS

SIMS



0.9 ‰

$$\Delta^{18}\text{O}_{\text{SIMS-GSMS}} = -0.9 \text{ ‰, at relatively low and constant OH/O}$$

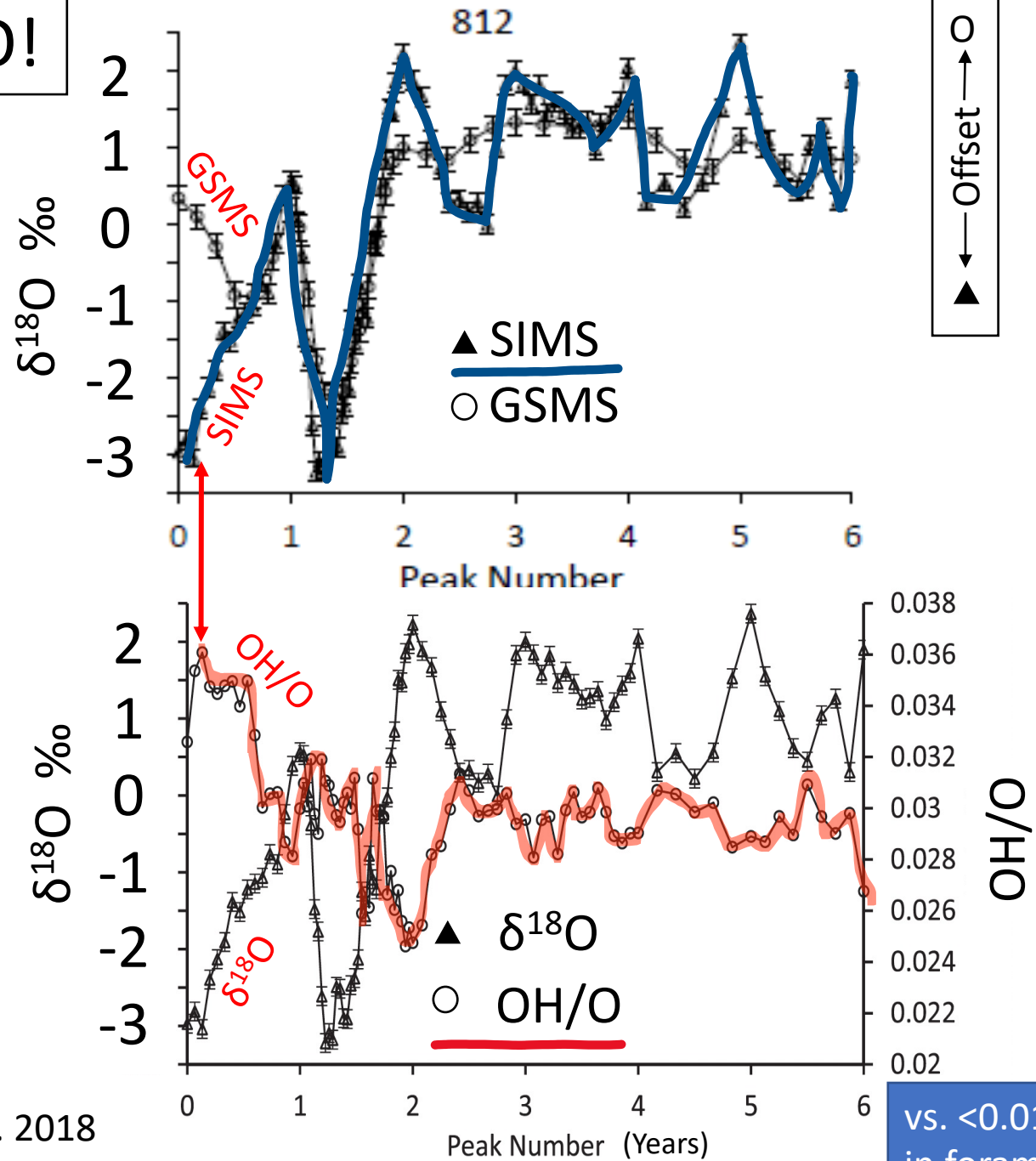
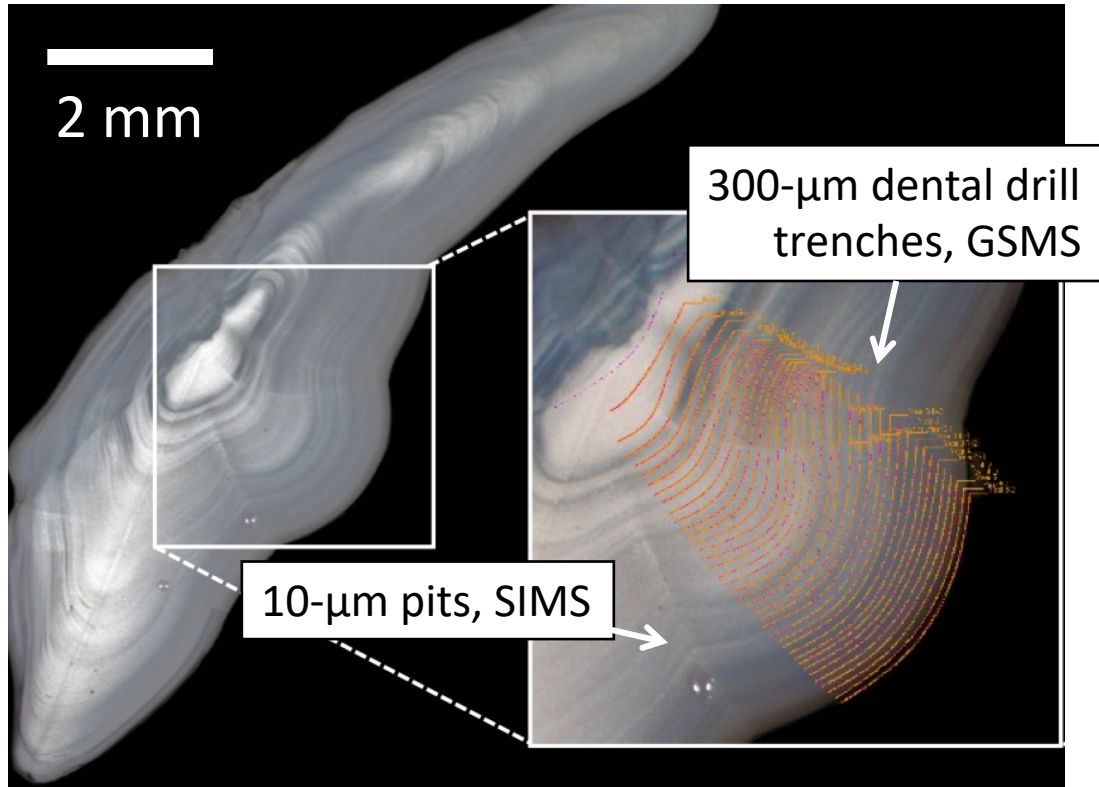
This offset is specific to sample type and instrument parameters.

Wycech et al. 2018



BEWARE of variable high & OH/O!

P. cod Otoliths, Bering Sea
 Aragonite, data logger (T, P, time)
 Protein-rich summer growth, opaque
 Protein-poor winter growth, dense & translucent

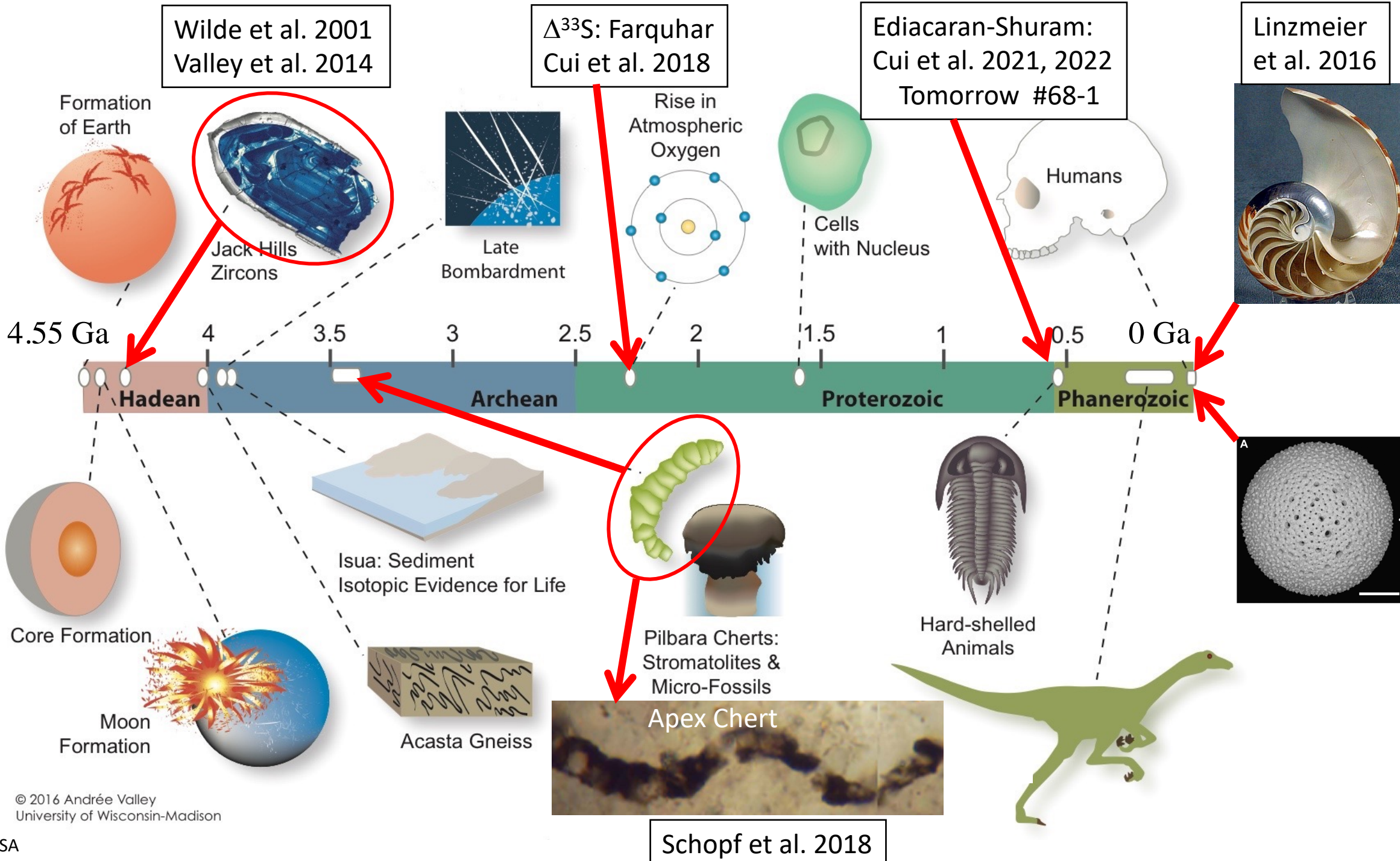


vs. <0.01‰
 in forams



NOAA
 FISHERIES

Helser et al. 2018



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University of Wisconsin-Madison

Valley 2022 GSA



Small, precious or zoned

Precision: varies with spot size, evaluate with running standards

Accuracy: sample preparation, RMs should match samples

